Evidence for the origin of monoalkenes in cigarette smoke

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Among the known chemical constituents of tobacco smoke are six homologous series of monoalkenes.[1] These series contain *cis*- and *trans*-isomers of *n*-, *iso*-, and *anteiso*-alkenes, having 10 to 32 carbon atoms. The suggestion has been made[1] that these alkenes may arise from pyrolysis of alkanes, acids, esters or ketones within a burning cigarette, since the alkenes are not known tobacco leaf constituents and do not show the quantitative differences between homologues with odd and even numbered carbon atoms characteristic of many plant constituents. In this communication, observations are reported on possible precursors for the pyrosynthesis of alk-1-enes.

Previous investigations[2–5] have implicated the tobacco leaf paraffins in the pyrosynthesis of polynuclear aromatic hydrocarbons (PAH) at temperatures usually exceeding 800°c, which approximates to the burn temperature of a cigarette (Table). However, since a sharp temperature gradient occurs in a narrow region behind the burning cone of a cigarette, the pyrolytic patterns of tobacco leaf paraffins and related compounds at lower temperatures, *e.g.* 650°c, have been studied in order to determine the role of these compounds as possible precursors of known smoke constituents other than PAH. Pyrolysis of tobacco leaf paraffins at 650°c under nitrogen, yielded minor quantities of simple aromatic hydrocarbons and, as major products, an apparent homologous series of aliphatic hydrocarbons based on gas chromatographic behaviour. Further work on some members of this series resulted in identification of the C_7-C_{17}-alk-1-enes based on spectral (infrared and mass) and gas chromatographic characteristics. In addition, the presence of higher homologues (C_{18}-C_{32}) of this series was indicated by gas-chromatographic retention data. Moreover, we also pyrolysed under identical conditions individual paraffins of varying chain lengths representative of compounds of tobacco leaf. Dotriacontane, docosane, and octadecane each yielded a homologous series of alk-1-enes, the highest member of which possessed one less carbon atom than the pyrolysed paraffin. Since the major leaf paraffins are in the C_{25}-C_{35} range,[6,7] these results indicate that the paraffins may be precursors of the alk-1-enes in the $\leqslant C_{34}$ range found in cigarette smoke. To date, however, the highest homologue conclusively identified in cigarette smoke is the C_{32} monoalkene.[1]

Table

Products[a] *from pyrolysis of dotriacontane*

at 860°c	*at* 650°c
Benzene	Benzene
Alkylbenzenes	Alkylbenzenes
Indene	Alk-1-enes[c]
Naphthalene	
Alkylnaphthalenes	
Acenaphthylene	
Acenaphthene	
Biphenyl	
Fluorene	
Anthracene/Phenanthrene	
Alkylanthracenes/Alkylphenanthrenes	
Fluoranthene	
Pyrene	
Benzo(*a*)pyrene[b]	

[a] In order of gas chromatographic retention times except as noted (see Ref. 4, 5)

[b] Identified by ultraviolet spectral properties of isolate from t.l.c. separation of pyrolysate (see Ref. 4, 8)

[c] $Me(CH_2)_nCH{=}CH_2$, $n = 4$–26, 27, 28. The compounds are the predominant products in the mixture obtained at 650°c

On the basis of the above and previous[5] observations, it would appear likely that the leaf paraffins contribute to at least three classes of cigarette smoke constituents as a function of temperature: aromatic hydrocarbons formed by pyrosynthesis at the temperature of the burning cone; monoalkenes and lesser amounts of simple aromatic hydrocarbons produced at the lower temperatures behind the burning cone; and paraffins released into the smoke stream by distillation at an even lower temperature (see Fig.).

Dotriacontane $\xrightarrow{860°c}$ Aromatic hydrocarbons, especially polynuclear aromatics

Dotriacontane $\xrightarrow{650°c}$ Homologous series of alk-1-enes (plus benzene and alkylbenzenes)

Dotriacontane $\xrightarrow{450°c}$ Dotriacontane

Fig. *Thermal effects on a representative tobacco leaf paraffin*

In related work, pyrolysis of stearic acid at 650°c (N_2) resulted in a homologous series of monoalkenes, the highest member of which was apparently heptadec-1-ene. Similar results were obtained from pyrolysis of the docos-1-ene which yielded alk-1-enes having $\leqslant 21$ carbon atoms. Although further studies are indicated, these results substantiate that pyrolysis of materials possessing long carbon chains can give rise to alkenes at 650°c. When the chain is not saturated, the position of the olefin linkages is apparently a critical factor in determining the point of scission in the chain; for example, oleic acid and octadec-9-ene, on pyrolysis, produced no alkenes above C_9.

In addition to the tobacco leaf constituents discussed above, long chain alcohols may very well play an important role in the formation of the alkenes present in cigarette smoke. Investigations along this line are currently being contemplated.

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